Exploring the Effect of EBC Composition on CMAS Wetting Behavior

[a,b] Clark Luckhardt, [b] Jamesa Stokes, [a] Elizabeth Opila

[a] Materials Science & Engineering, University of Virginia, Charlottesville, VA, USA

[b] NASA Glenn Research Center, Cleveland, OH, USA

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Engineering Ceramics Division
The American Ceramic Society

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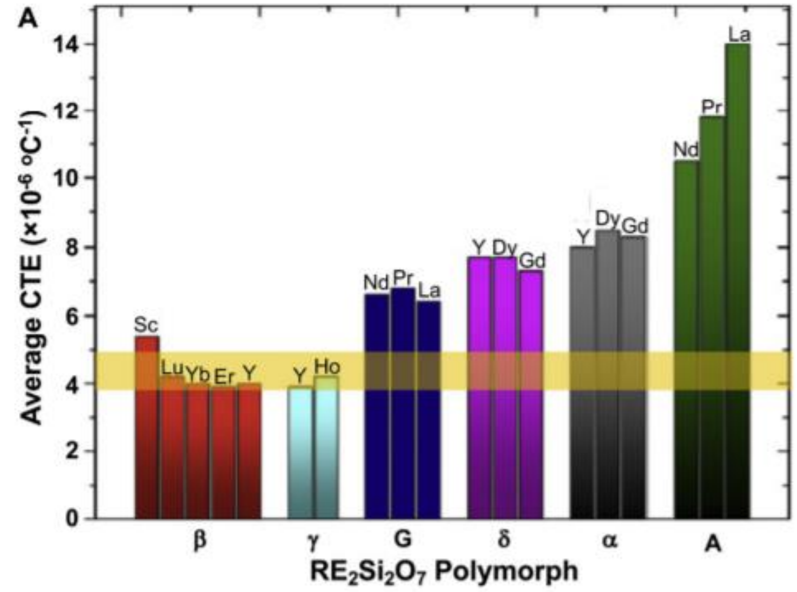
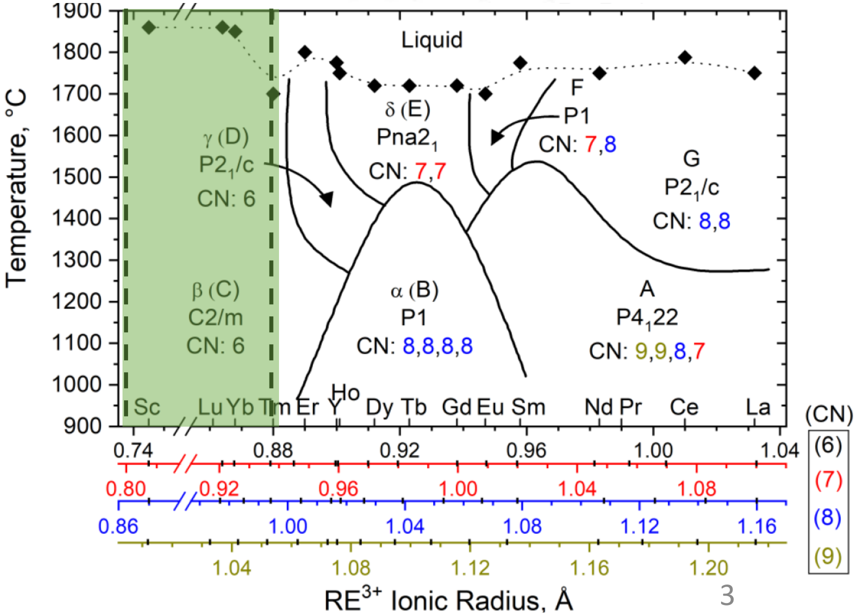
REDS as EBC Candidates

- $RE_2Si_2O_7$ (REDS; RE=Lanthanides, Sc, or Y)
  - 7 high temperature polymorphs
  - Good CTE match with SiC CMC (4.5-5.5x10^{-6}°C^{-1})
- No phase transformations in β-phase (Structure C), desirable for thermal cycling
- Literature shows research in evaluating feasibility of mixing REDS as EBC candidates
  - Y Dong et al., (2019); J Deijkers Dissertation (2020)
  - Motivates investigation of phase-pure REDS
- $Yb_2Si_2O_7$ (YbDS) state-of-the-art material



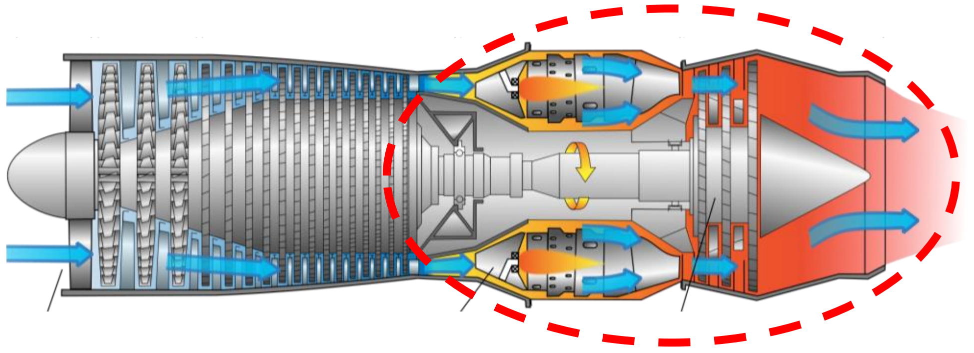


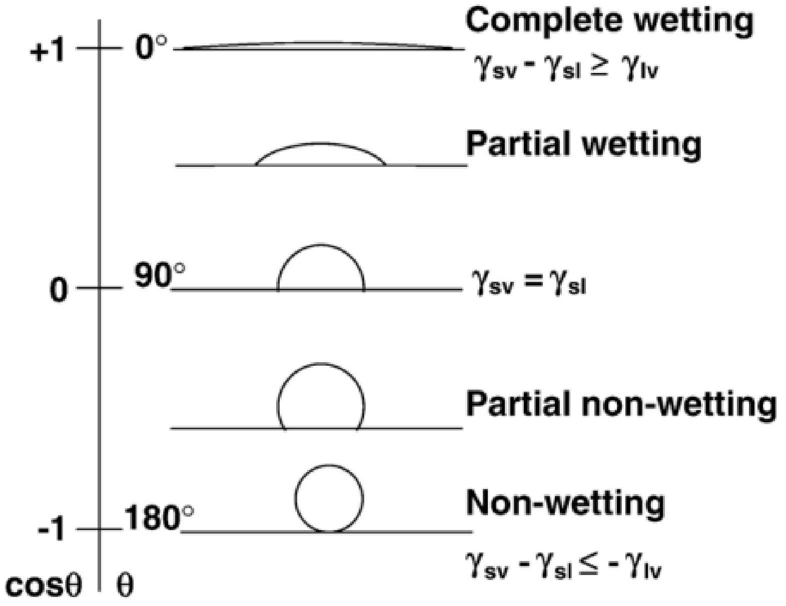
AJ Fernández-Carrión et al., *J. Am. Ceram. Soc.* (2013); Adapted by M Ridley from: J Felsche, *J. Less-Common Met.* (1970)

CMAS Wetting of EBCs

- Stationary vanes and stators in engine hot section prone to molten CMAS attack
- Substrate material can affect wetting
    - Surface roughness
    - Heterogeneity
    - Reactivity
- Degree of wetting governed by contact angle at equilibrium
    - Measure of liquid's adhesive forces

$$\cos\theta = \frac{\gamma_{SV} - \gamma_{SL}}{\gamma_{LV}}$$





sv = solid-vapor; sl = solid-liquid; lv = liquid-vapor

https://en.wikipedia.org/wiki/Components_of_jet_engines; G. Kumar & N. Prabhu, *Advances in Colloid and Interface Science* (2007)

Knowledge Gap, Objective, and Hypothesis

No *published* CMAS wetting studies done on rare-earth silicates, but some studies performed on rare-earth phosphates. No literature on effect of REDS processing, composition, or porosity on CMAS wetting.

Study the effects of coating composition and morphology on CMAS wetting through quantifying CMAS contact angle and spreading.

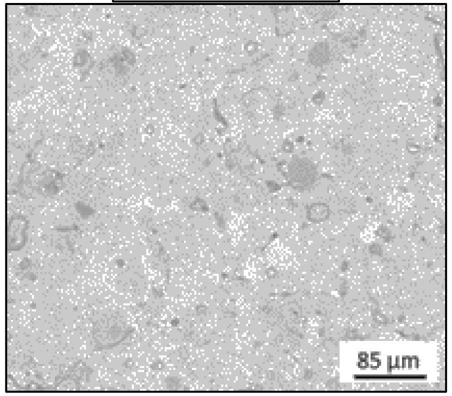
Contact angle evolution is expected to change with rare-earth reactivity, trending with stability in the rare-earth apatite structure.

Cite literature on REPO4 wetting study

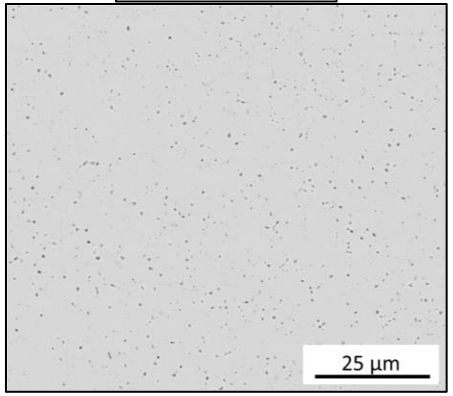
Materials

- Atmosphere Plasma Spray (APS) $RE_2Si_2O_7$ (REDS)
  - RE = La, Nd, Gd, Yb, Lu, Y, (Y + Yb)
- Spark Plasma Sintered (SPS) YbDS
- SPS 20vol% Yb2SiO5 in YbDS
- All substrates were polished to grit 4000 (US #1200) and ~94-98% dense
  - Three trials of at least 2 h; one of 4 h
- 0.73 Ca:Si CMAS, from Krämer et al.
  - $33CaO – 9MgO – 13AlO_{1.5} – 45SiO_2$

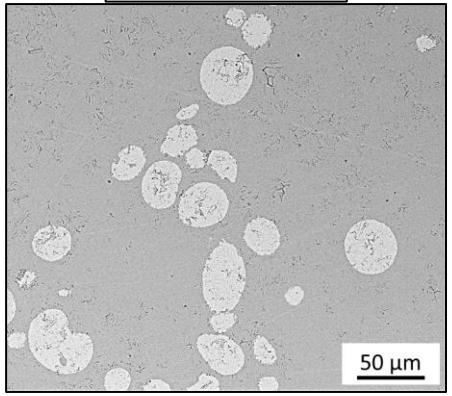
APS YbDS



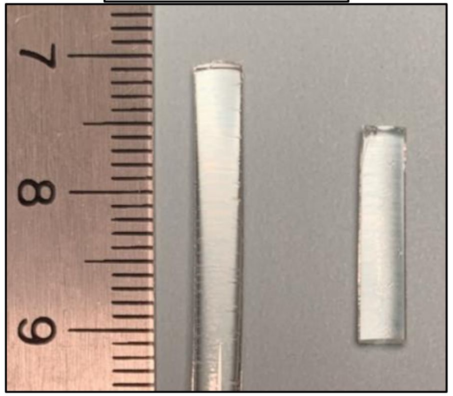
SPS YbDS



SPS Mixed



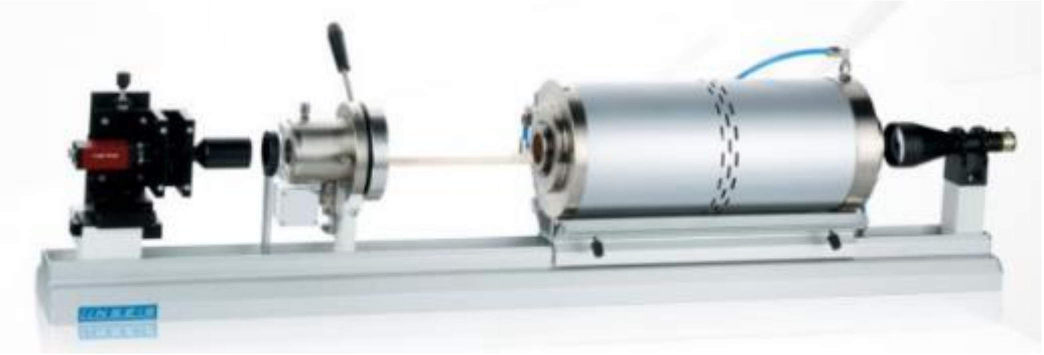
CMAS Rod



Krämer et al., *J. Am. Ceram. Soc.* (2006)

Methods – Equipment

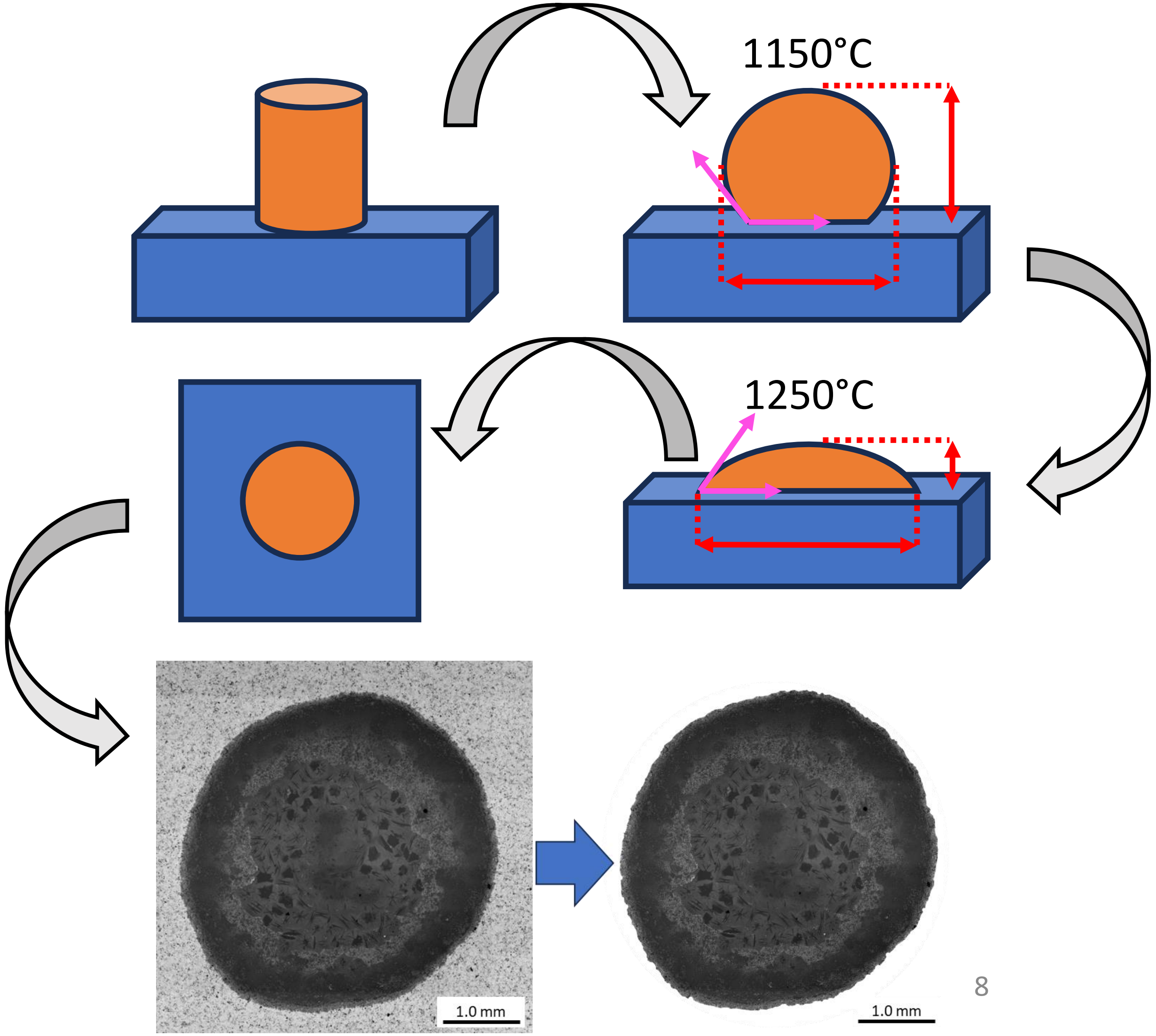
- Linseis L74/HS/1700 Heating Microscope
  - Performed in lab air
  - CCD camera capturing 2D image and measuring wetting angle
  - Each experiment measured two contact angles, width, and height
- CMAS glass rod sectioned into 10 mg cylinders
  - Held at 1250°C, three trials for 2h and one trial for 4h



Linseis L74/HS/1700 Hardware Manual; M Wilson, Dissertation (2018)

Methods – Data Collection

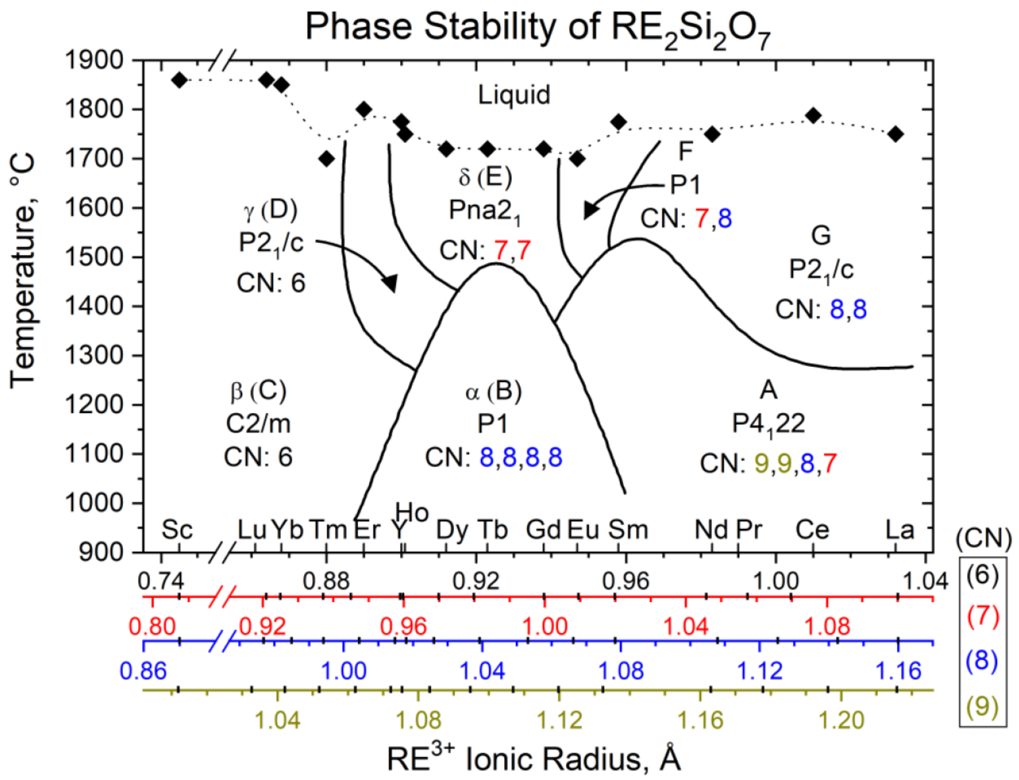
- Linseis L74/HS/1700 Heating Microscope
  - Contact angle, height, width
- Data collected
  - On heating at 1150°C to evaluate unreacted surface interactions
  - Held at 1250°C, three trials for 2h and one trial for 4h
- Quantify CMAS spreading using plan view SEM and ImageJ analysis



Linseis L74/HS/1700 Hardware Manual; M Wilson, Dissertation (2018)

RE Cation Size (Å) Dependence on Coordination Number

Species (3+)	CN6	CN7	CN8	CN9
La	1.032	1.1	1.16	1.216
Nd	0.983	---	1.1.09	1.163
Gd	0.938	1	1.053	1.107
Yb	0.868	0.925	0.985	1.042
Lu	0.861	---	0.977	1.032
Y	0.9	0.96	1.019	1.075



Rare earth cation size changes depending on coordination behavior in each structure

http://abulafia.mt.ic.ac.uk/shannon/ptable.php; Adapted by M Ridley from: J Felsche, *J. Less-Common Met.* (1970)

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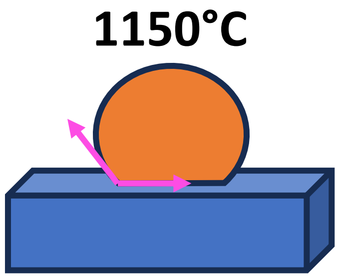
Species	CN#	Ave CN
LaDS	9,9,8,7	1.173
~~NdDS~~	~~9,9,8,7~~	~~No CN7~~
NdDS	8,8	1.109
GdDS	8,8,8,8	1.053
YbDS	6	0.868
LuDS	6	0.861
YDS	6	0.9
(Y+Yb)DS	6	0.884
Yb(20MS/DS)	Mix	0.875

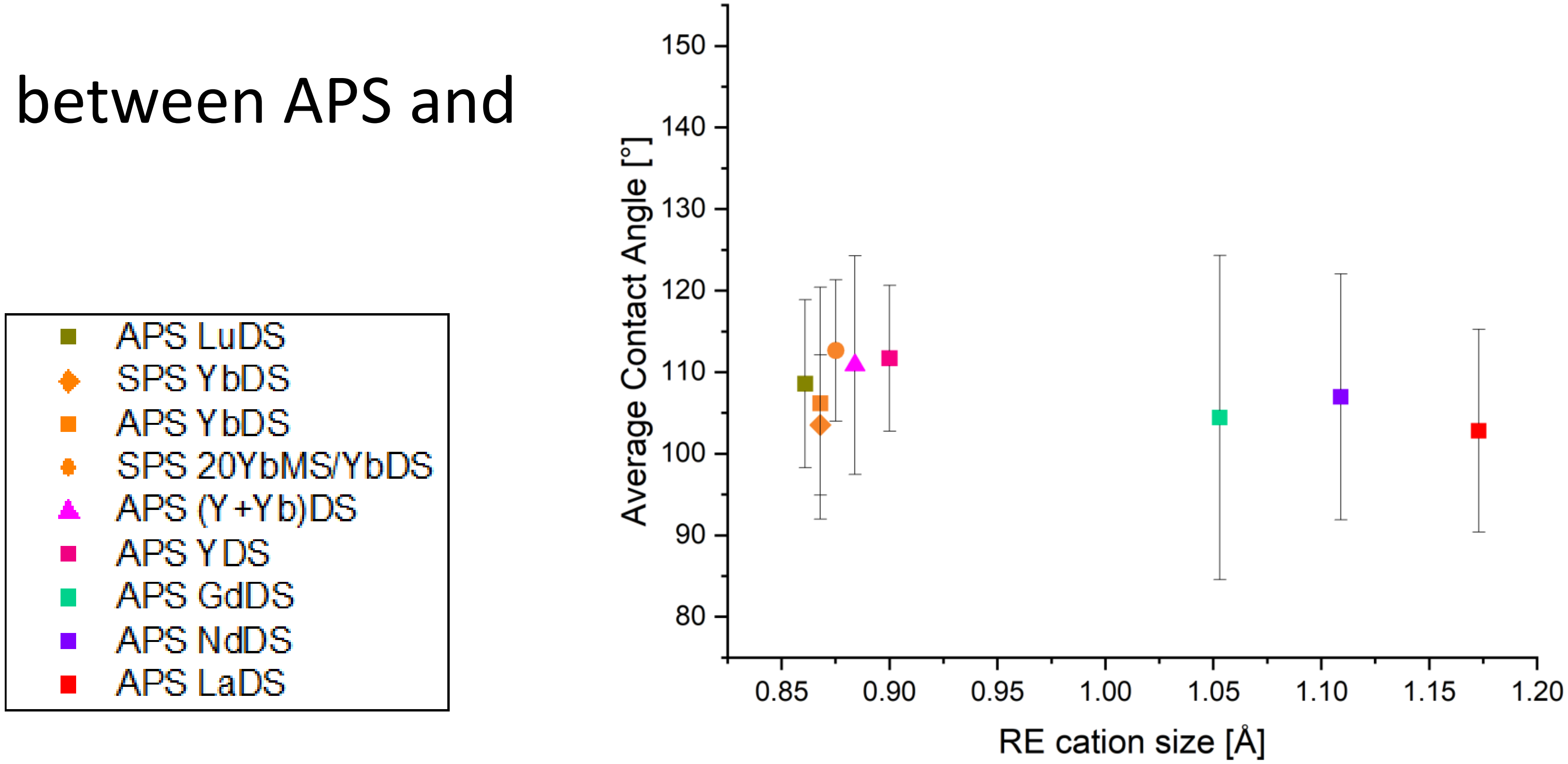
Used the rare earth cation size for the expected coordination behavior in each structure

http://abulafia.mt.ic.ac.uk/shannon/ptable.php; Adapted by M Ridley from: J Felsche, *J. Less-Common Met.* (1970); https://next-gen.materialsproject.org/materials/mp-5974; https://next-gen.materialsproject.org/materials/mp-556771; https://legacy.materialsproject.org/materials/mp-4300; H Xiang et al, *J. Mat. Research* (2014)

Contact Angle Evolution

- No significant differences in contact angle at 1150°C
- Similar behavior between APS and SPS Yb-silicates

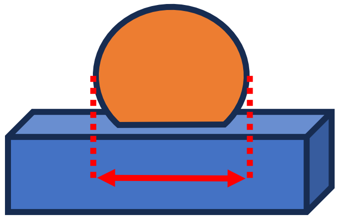


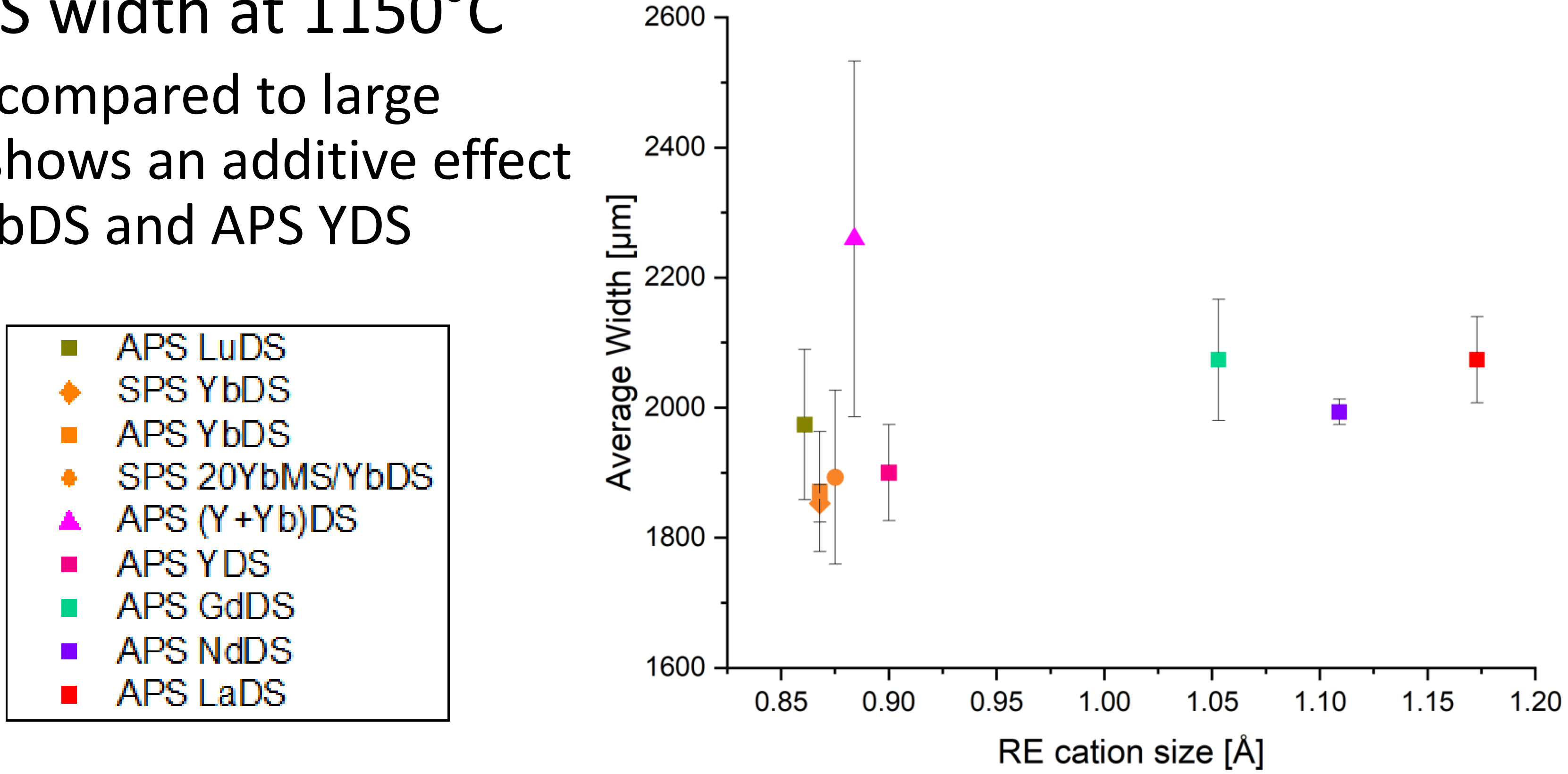


Width Evolution

- APS (Y+Yb)DS shows an initial increase in CMAS width at 1150°C
  - Not significant compared to large cation RE, but shows an additive effect between APS YbDS and APS YDS

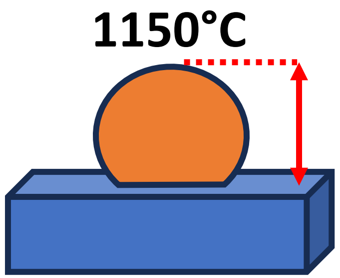
1150°C

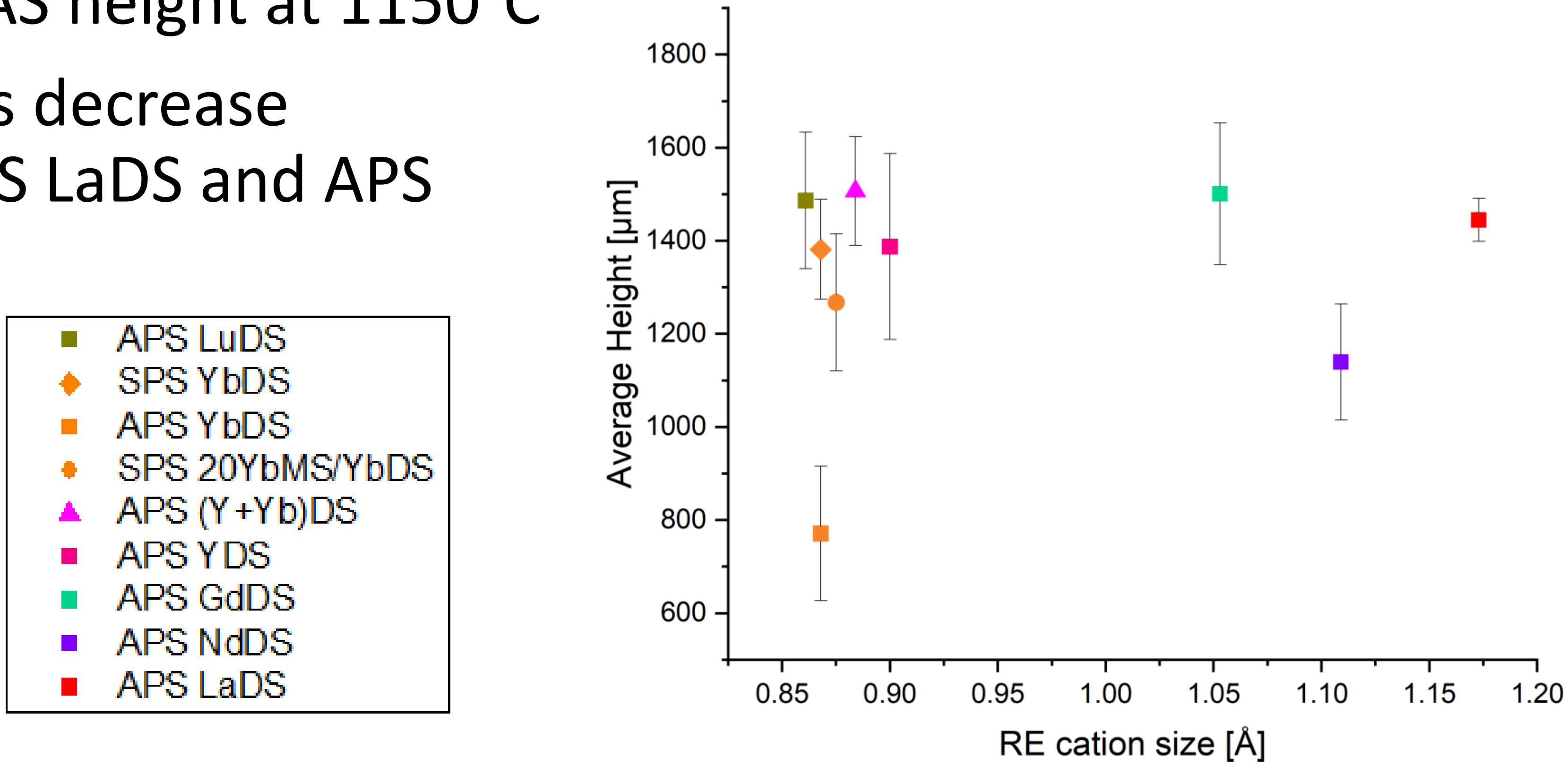




Height Evolution

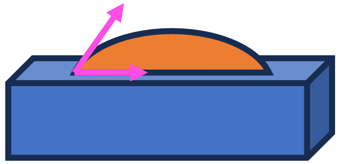
- APS YbDS shows significant decrease in CMAS height at 1150°C
- APS NdDS shows decrease compared to APS LaDS and APS GdDS





Contact Angle Evolution

1250°C



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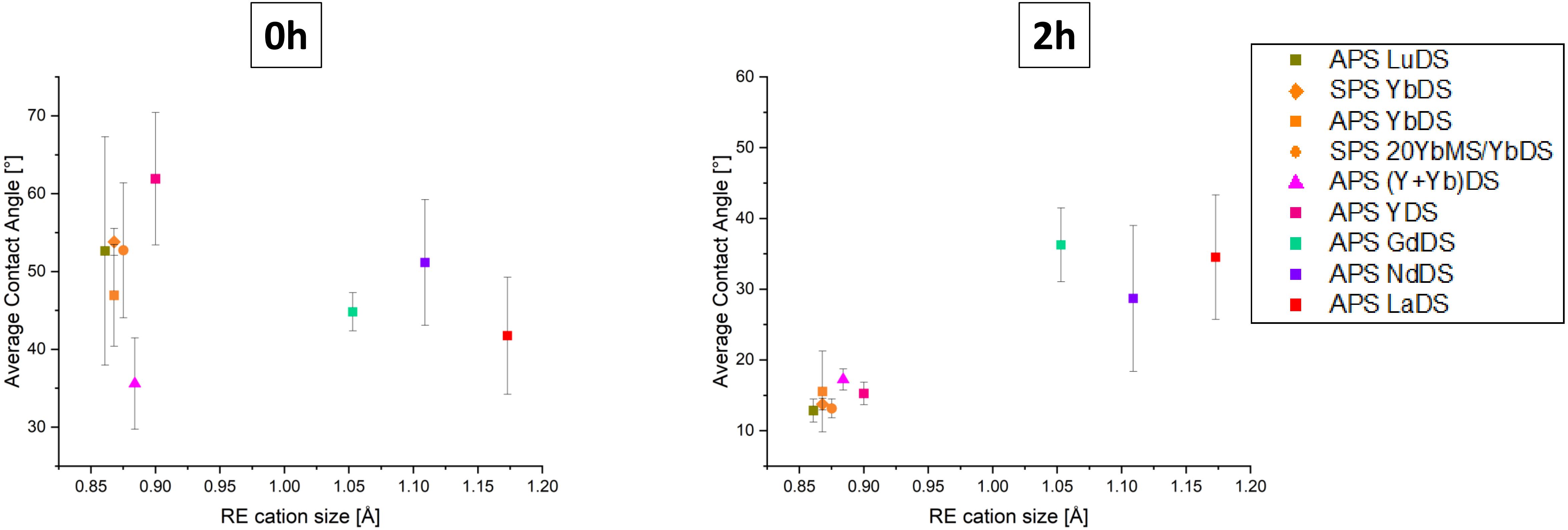
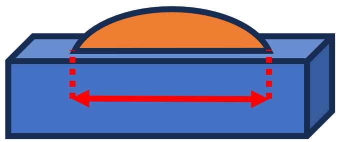
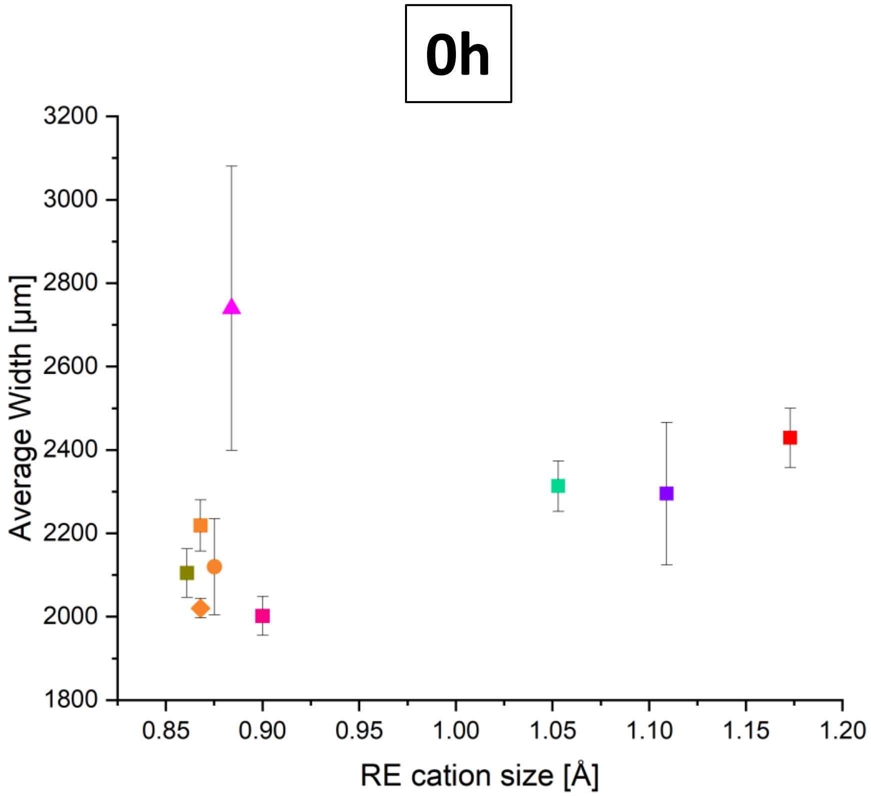


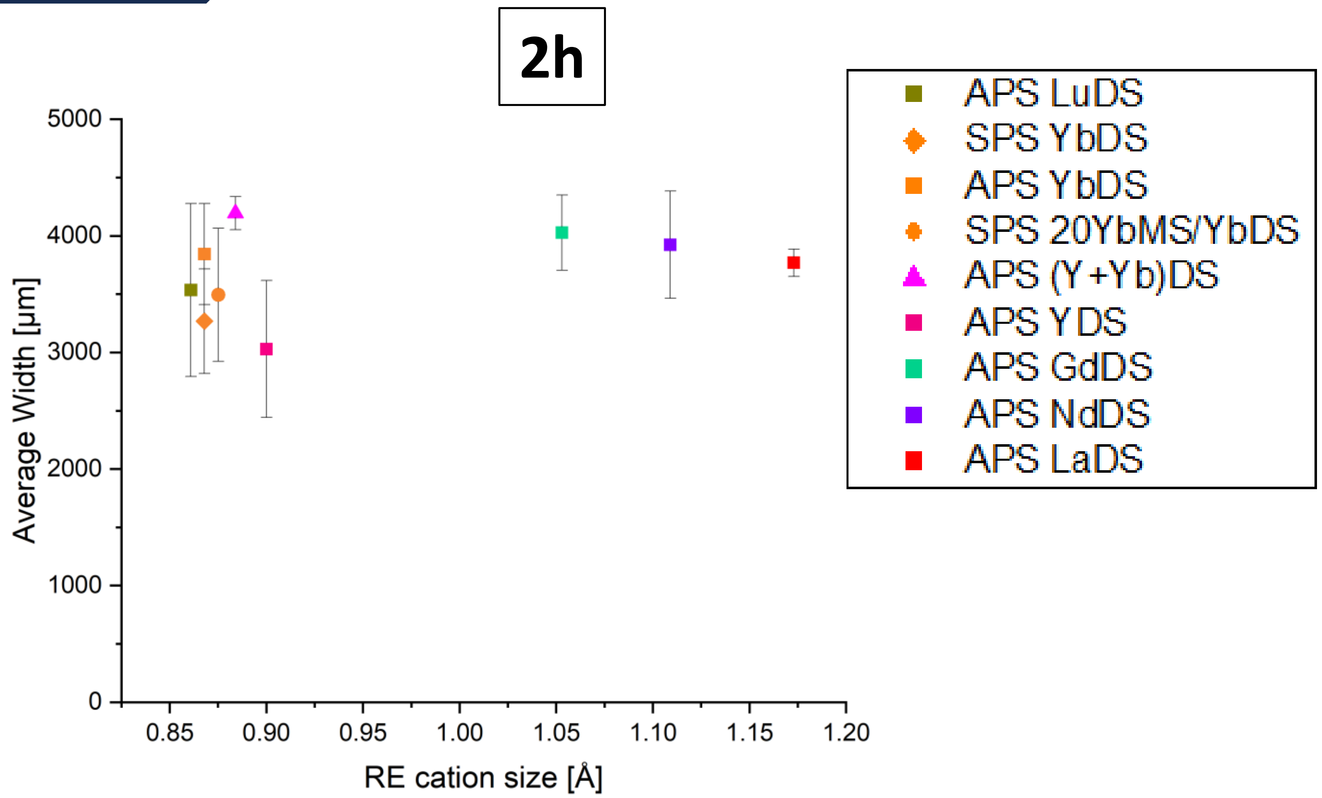
- No significant differences at 1250°C (0h)
- After 2h there is clear separation between small and large RE cations

Width Evolution

1250°C



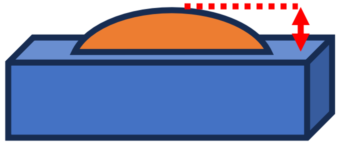


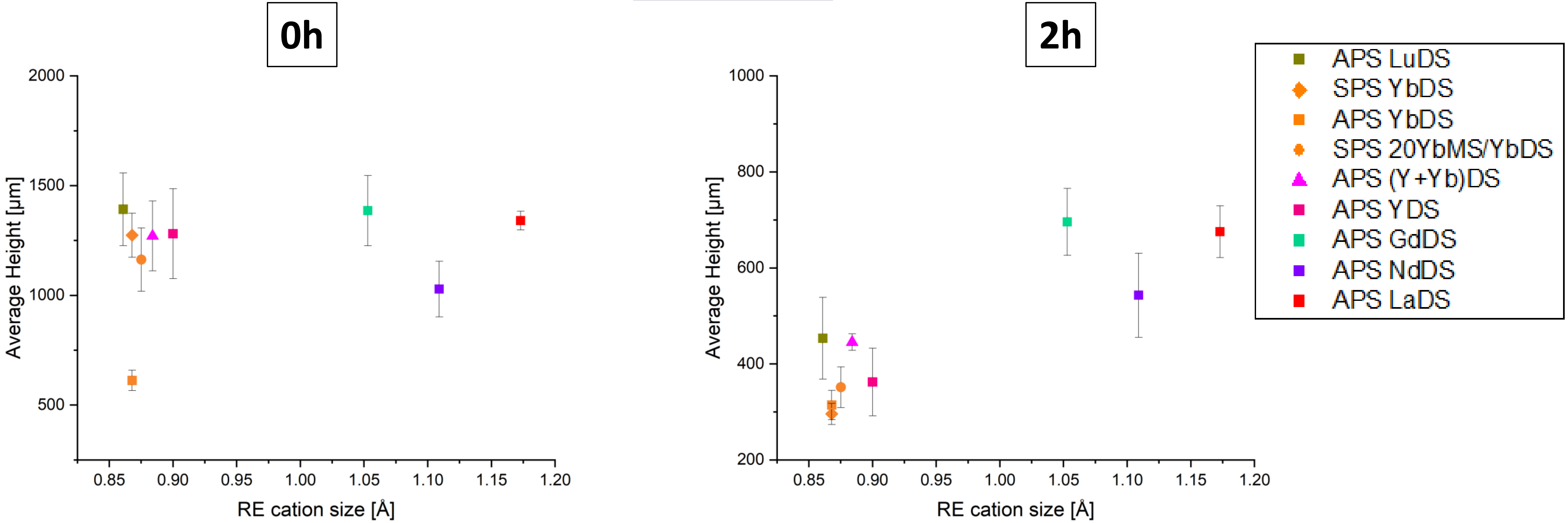


- APS (Y+Yb)DS shows an initial increase in CMAS width at 1250°C (0h)
- After 2h there is no significant difference between substrates

Height Evolution

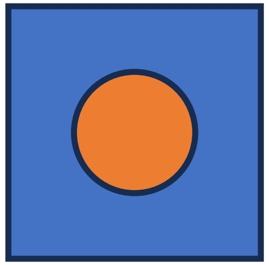
1250°C





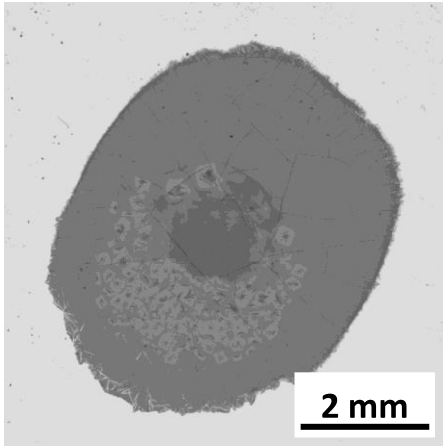
- APS YbDS shows initial decrease in height at 1250°C (0h)
- After 2h there is clear separation between small and large RE cations

CMAS Spreading

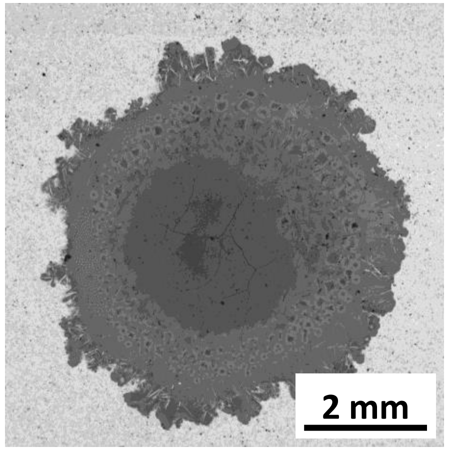


- Heating microscope data does not tell full story
  - Becomes obvious when observing samples in plan view
  - Non-uniform wetting perimeters are not accounted for in width measurements
- Thresholding in ImageJ allowed for quantification of CMAS spreading

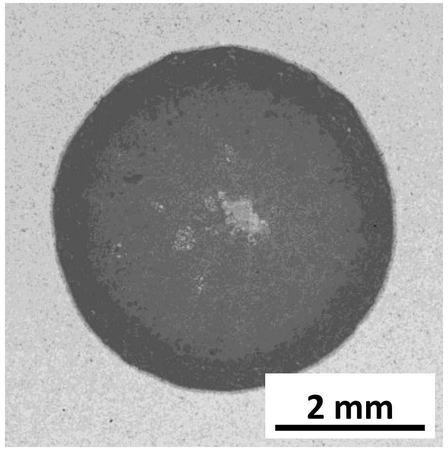
SPS YbDS, 1250°C, 2h



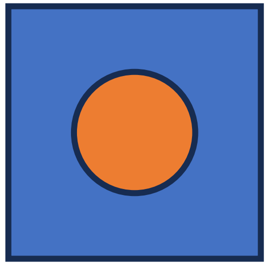
APS LuDS, 1250°C, 2h



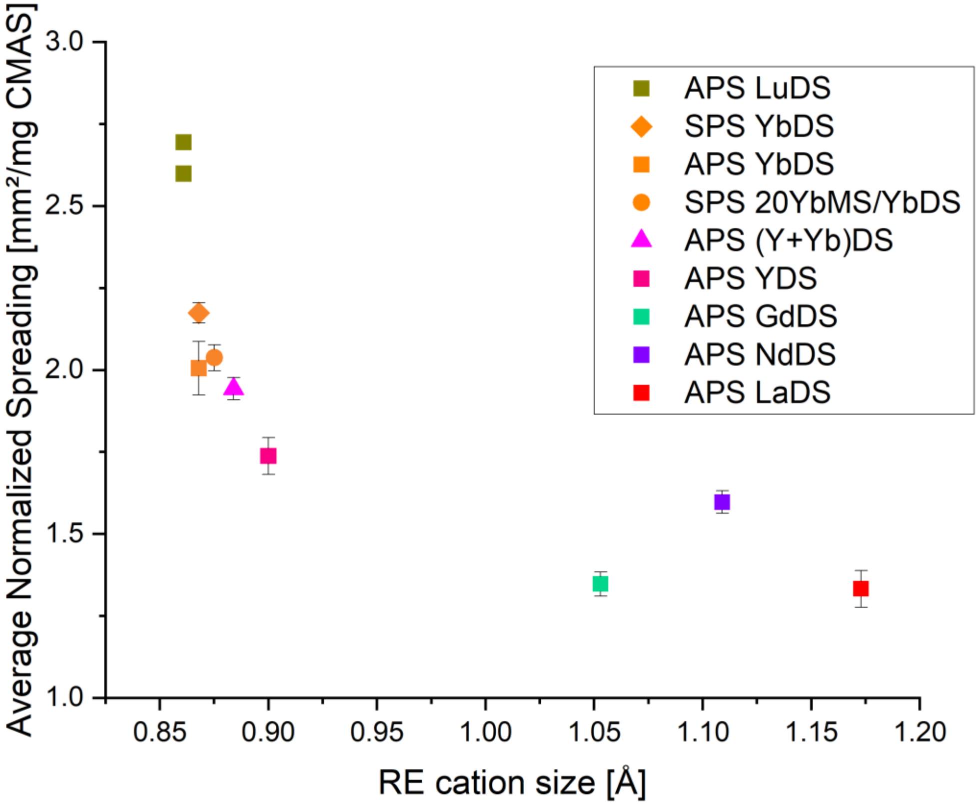
APS NdDS, 1250°C, 2h



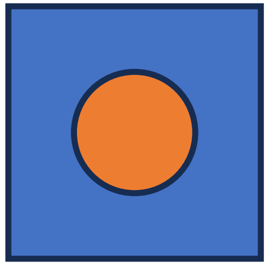
CMAS Spreading

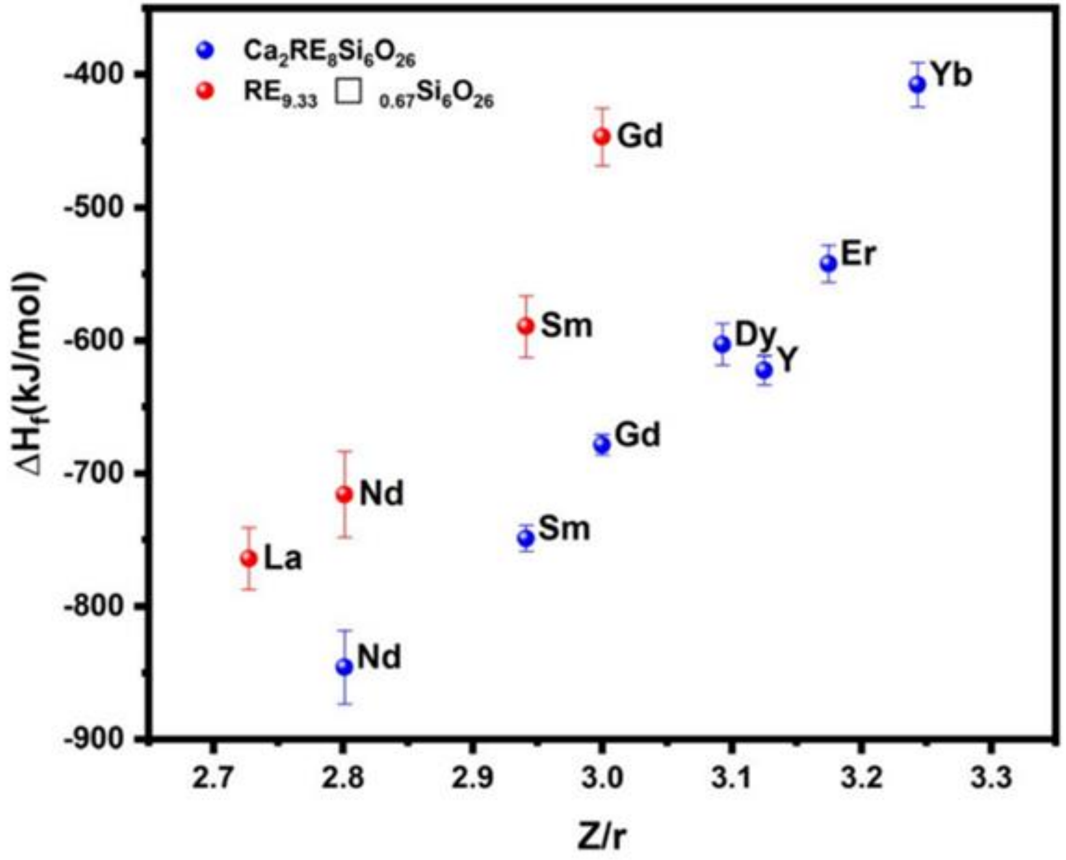


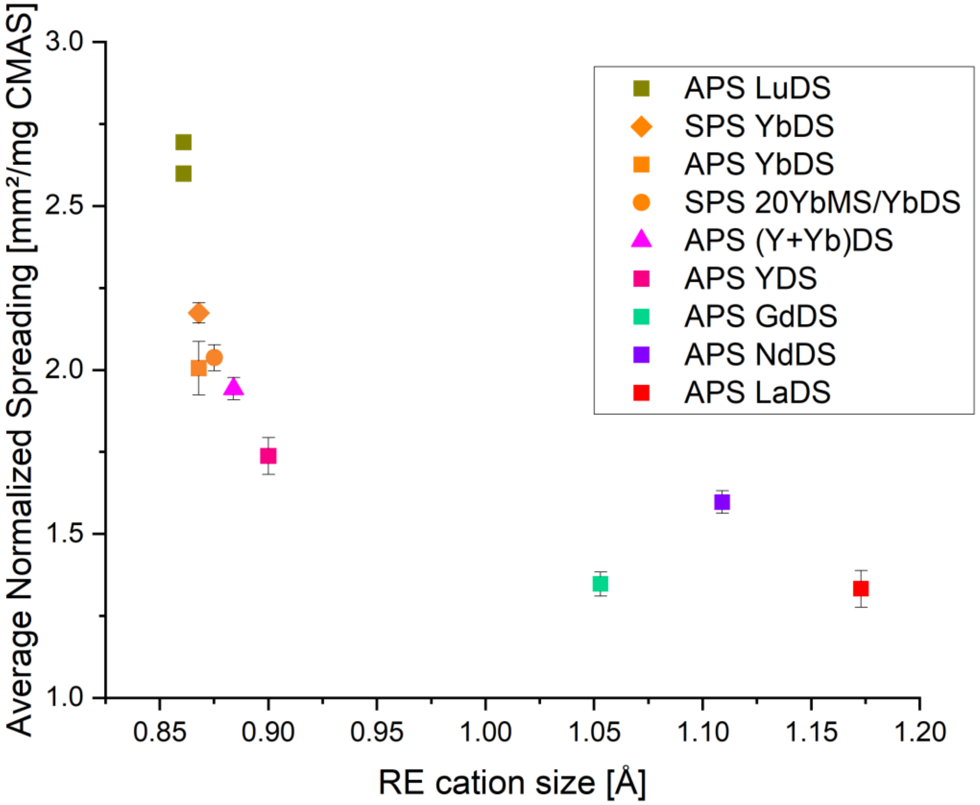
- Plotted are the average areas of CMAS spreading (mm^2) normalized by the CMAS load (mg)
  - For the three samples exposed for 2h
- SPS YbDS shows more spreading than the APS YbDS and SPS 20YbMS/YbDS
- Larger RE cation size, less spreading
  - Except for APS NdDS
- **Shows the need to observe CMAS wetting in each dimension**



CMAS Spreading







CMAS spreading on single cation REDS correlates with RE-apatite stability

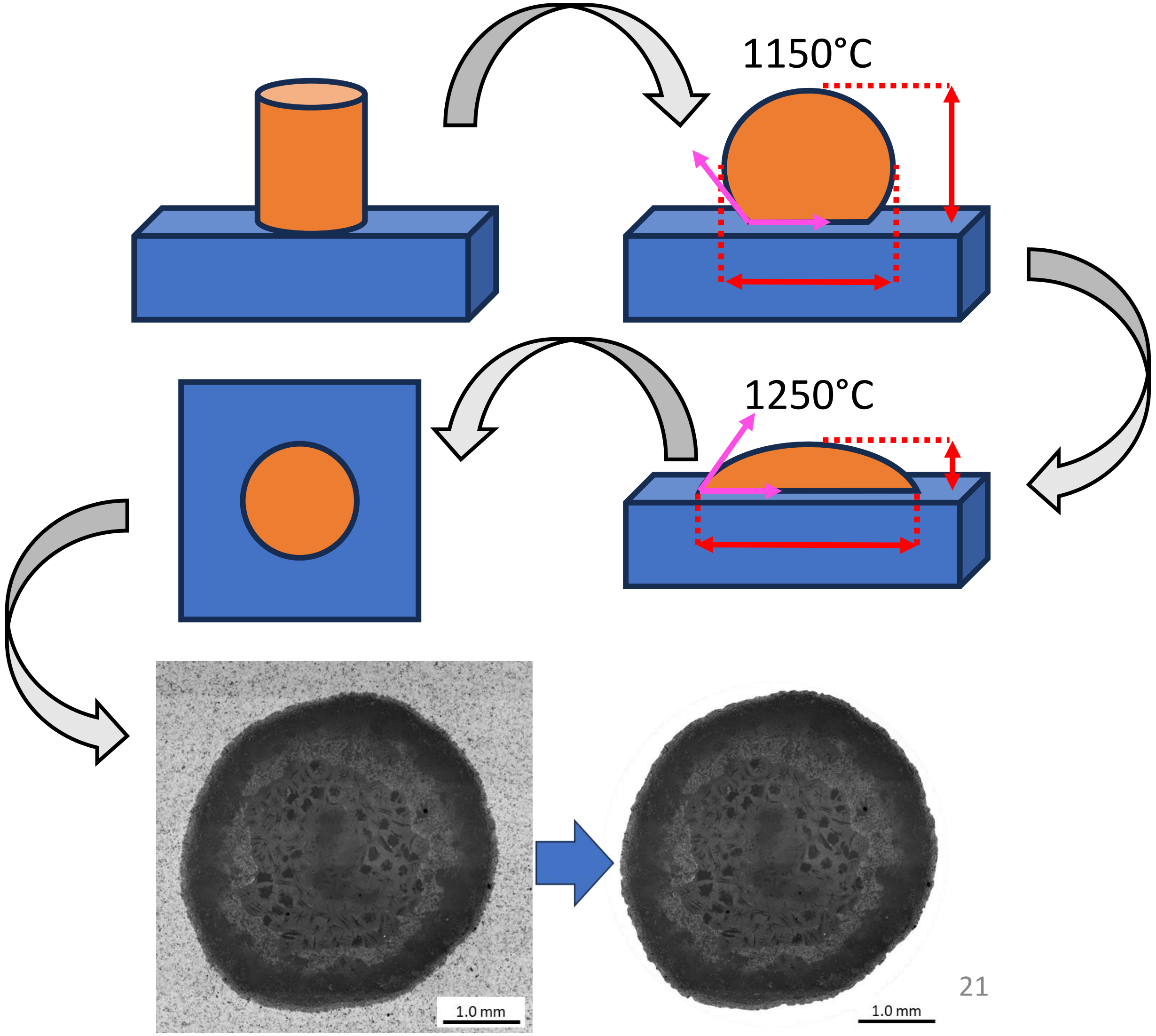
AS Risbud et al., *J. Mater. Res.* (2020); G Costa et al., *J. Am. Ceram. Soc.* (2020)

Summary & Conclusions

- Contact angle showed weak dependence on apatite stability
  - Larger cation sizes produced larger contact angles and after 2h at 1250°C
- APS YbDS specimens displayed lower CMAS heights at early stages of the experiment
  - No other significant differences occurred in APS and SPS Yb-silicates samples
- Wetting microscope does not capture the whole picture
  - Plan view analysis incorporates non-uniform wetting phenomena and improves our understanding of REDS cation size effect on CMAS wetting
  - CMAS spreading on single cation REDS correlates with RE-apatite stability
- APS YbDS & SPS 20YbMS/YbDS reduced CMAS spreading vs. SPS YbDS

Future Work

- Investigating CMAS wetting on APS YbMS
- Investigating effect of porosity on CMAS wetting of APS YbDS
- Completing data analysis on 4h exposure length samples
- Cross-section analysis to quantify cation size effect on reaction product thicknesses and CMAS infiltration



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Thanks!